

# USE OF UNCORRECTED X-RAY DIFFRACTION DATA IN QUANTITATIVE ANALYTICAL DETERMINATIONS

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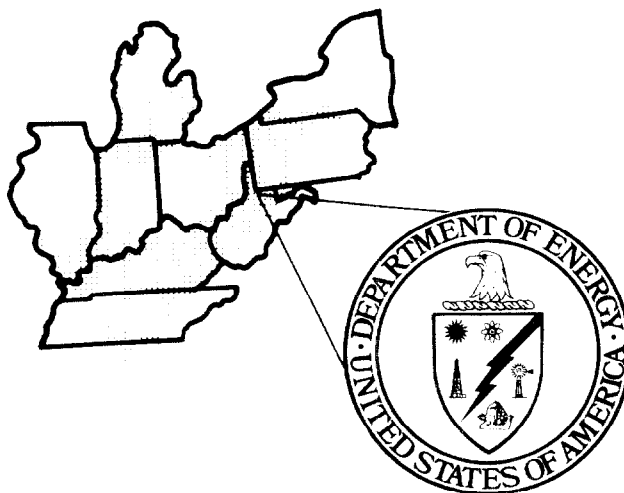
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for

**MORGANTOWN ENERGY RESEARCH CENTER**

**Morgantown, West Virginia 26505**

**Date Published - October 1977**

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DATA IN QUANTITATIVE ANALYTICAL DETERMINATIONS

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July 1977

ABSTRACT

Uncorrected X-ray diffraction data can be used to quantitatively determine the composition of a mixture of crystalline phases. As long as the samples are carefully prepared, the integrated intensity of a Bragg reflection from a sample is directly proportional to the concentration of the crystalline phase in the sample, and for most sedimentary mineral phases, the coefficient of proportionality is near unity. Because sample preparation is critical to the success of this approach, the sample preparation techniques used in this laboratory are presented in detail. The argument to substantiate the premise of this paper is in the form of five sets of data collected on suites of samples submitted by colleagues. The data represent a variety of analytical problems and will demonstrate that the percent total integrated intensity (%TII) values accurately estimate the true composition of the samples.

## INTRODUCTION

Most individuals with an analytical background are aware that X-ray diffraction data can be used to quantitatively determine the composition of a mixture of crystalline phases. They have learned that the integrated intensity of the Bragg reflections from any crystalline component in a mixture is a function of the volume percentage represented by that component. However, the relationship is not a direct one, and it is modified by a long list of "intensity correction factors," including:

1. Absorption of the incident and diffracted X-ray beams by the component itself and by the remaining components (the matrix),
2. The angle at which diffraction occurs,
3. Particle size of the sample, and
4. Orientation (or non-orientation) of the crystallites within the sample.

Admittedly, with the exception of the absorption factor, most of these are of minor influence in powder diffraction. The classic method of accounting for the major factors influencing the intensity-concentration relationship is to incorporate an internal standard in known concentration into each unknown sample, monitor the peak-intensity ratio between the desired analytical parameter and the internal standard, and then compare the ratio against a concentration-ratio plot acquired from a set of known standard samples containing the internal standard. All of these procedures are time consuming and no doubt discourage investigators from using the technique.

It is the premise of this paper that as long as the samples are carefully prepared, the integrated intensity of a Bragg reflection from a sample is directly proportional to the concentration of the crystalline phase in the sample producing the reflection, and that the coefficient of proportionality is near unity for most sedimentary mineral phases. The argument to defend this premise is in the form of five sets of analytical data in which the X-ray diffraction data are compared against compositional or compositional-dependent data generated by non-X-ray techniques.

## SAMPLE PREPARATION

In all analytical techniques, the quality of the data is only as good as the quality of the sample preparation. Because the basic X-ray data are not corrected, the sample-preparation phase of the analysis is highly critical to the success of the technique. For this reason, a detailed description of the sample-preparation procedures used in this laboratory is presented before the presentation and discussion of the analytical data.

## Rock Samples

Certain monomineralic rocks, such as quartz sandstones, do not lend themselves to direct X-ray diffraction analysis, because of the overwhelming abundance of a single-mineral phase. The following technique, therefore, is intended mainly for multi-major-component samples. Mono-component samples require special separation and concentration of the minor ingredients, and this is not discussed here.

The following procedure is used for the analysis of all rock samples. The original sample is crushed by any appropriate technique to a maximum particle size of about 0.1 mm. A representative portion of the crushed sample is then taken by use of a Jones splitter and transferred to a 65 ml Spex stainless-steel grinding vial, equipped with a cap compression-type closure. The vial is filled no more than one-third full with crushed sample. Approximately 20 ml of methanol are added, along with 300 1/8-inch stainless-steel grinding balls. (The methanol prevents thermal deformation of the crystal lattices and ensures homogeneity of the sample while grinding.) The vial is sealed and the sample is ground for 15 minutes on a Spex Mixer-mill grinder. At the end of the grinding period, the vial is opened and the resultant slurry is poured through a wire screen into an evaporating dish. The mesh size of the screen should be sufficient to trap the grinding balls but not interfere with the passage of the sample slurry. The vial, screen, and balls are then thoroughly washed with a stream of methanol and the slurry is set aside to dry, usually overnight.

This grinding technique was described by Diebold, Lemish, and Hiltrop (1963) where they indicated that calcite was reduced to less than 10-micron particle size within 5 minutes of grinding. They indicated that a 5-minute grinding period (with calcite) produced comparable results to the reduction by hand-grinding to 325 mesh followed by 15 hours of wet-ball milling under alcohol. Studies conducted in this laboratory verify this statement. Calcite samples prepared for infrared analysis were reduced to a median size of 8 microns within 15 minutes using this grinding technique.

During the drying process, there will always be a certain amount of preferential settling based on particle density and size. This is minimized by initially using only that amount of methanol which produces a moderately thick slurry at the end of the grinding. When the sample has thoroughly dried, the resultant cake is hand-pulverized and reblended to ensure homogeneity. (It is here that minimizing the initial preferential settling is important.) Once the sample is thoroughly blended, a portion is transferred to a Spex-cap and the cap is tapped lightly to compact the sample. The cap and sample are then pelletized.

If there is enough sample to fill the bottom of the Spex-cap to a millimeter or two, a pellet can be made successfully.

If, however, there is insufficient sample to cover the bottom of the Spex-cap, the cap is filled with powdered boric acid, the acid is firmly tamped into place, and the surface is smoothed. The sample is then carefully dusted onto the surface of the acid. The cap with the acid and sample is then pelletized.

All pellets are made by subjecting the pellet to 10 tons total load for 2 minutes. The pressure is then released, the die is rotated 180°, and the pressure is reapplied for an additional 2 minutes. The pellet is then removed, placed into an envelope, and stored in a desiccator until the analysis is performed. (In the absence of adequate desiccator space, the pellet envelopes can be stored in "zip loc" plastic bags into which dessicant is placed.)

On occasion, especially with some samples rich in clay minerals, the sample surface will adhere to the surface of the upper platen when the pellet is removed from the die. This problem can be solved with the following procedure. Before making the pellet, the lower platen is centered on the die anvil. The filled Spex-cap is carefully centered on top of the lower platen. A 1 ½-inch square piece of "Saran wrap" or equivalent is placed on top of the Spex-cap, and the body of the die is carefully lowered around the Spex-cap and lower platen, care being taken not to dislodge the plastic wrap. The upper platen is then lowered into place along with the plunger, and the pellet is made following the previously described procedure. When the pellet is removed, the plastic wrap is carefully removed from the sample surface.

#### Insoluble Residues and Clay Materials

Rocks which contain significant amounts of carbonate minerals are usually subjected to an acid-insoluble-residue determination, in addition to the whole rock analysis. Once prepared, the residue is also subjected to X-ray diffraction analysis.

The acid-insoluble residue is prepared by weighing approximately 1 gram, to the nearest milligram (or ½ gram in the case of a high-residue carbonate or a calcareous noncarbonate). The weighed sample is transferred to a 250 ml beaker and wetted with sufficient distilled water to make a thin slurry. Fifty milliliters of 0.5N HCl is then slowly added while stirring. When all reaction has subsided, an additional 50 ml of acid is added, and the sample is allowed to digest overnight. If the sample is known to contain dolomite, the sample is placed on a warm hotplate for the digestion period.

When the digestion is complete, the sample is mounted onto a 47 mm Millipore filter by vacuum-filtering the suspension through a Millipore Sterifit vacuum-filtering system. The filter mounting is a general procedure used in this laboratory for most non-lithified samples, but especially for acid-insoluble residues and clay-mineral suspensions.

In the case of the acid-insoluble residue, the suspension is quickly poured into the Millipore filtering assembly, into which has



been placed a pre-weighed 47 mm filter. The filtering assembly is maintained under vacuum. Transfer of the sample should be as fast and as complete as possible to minimize preferential settling onto the filter surface. The filtered residue is then carefully washed several times with distilled water, care being taken not to disturb the filter cake. The vacuum is then shut off and the filter carefully removed from the assembly and placed between two paper towels to dry slowly. If the residues are allowed to dry too rapidly, or if they are too thick, the cake may crack and curl. Should this occur after the residue has thoroughly dried and has been weighed to attain the residue weight, the residue can be scraped off the filter and resuspended in pH10 water. An appropriate volume of the suspension can then be removed with a syringe and refiltered by the previously described process.

Usually, when a suite of samples is being prepared for residue determination, the original weight of sample needed to produce the proper thickness of residue on the filter can be estimated, based upon experience. For clay-mineral studies, a certain sediment concentration-per-unit area may be desired on each specimen mount; this may be accomplished by controlling the original clay-suspension concentration.

The resultant mount has been found to provide excellent clay-mineral orientation, comparable to those of the pressed-pellet technique. In the case of general clay-mineral analyses, it is assumed that any treatments to which the clay is to be subjected, such as heat or glycolation, have been performed prior to the filtering. (Heat treatments cannot be performed on filter-mounted samples.) The dried filters are prepared for X-ray diffraction analysis by carefully mounting the filters onto the surface of 40 mm square glass plates coated with a thin film of petroleum jelly. A statistical evaluation of the precision and accuracy of this and other X-ray sample-preparation techniques, as they pertain to the mineralogical analysis of shales, was reported by Cubitt (1975).

## X-RAY DIFFRACTION ANALYSIS

Normally a preliminary diffractogram is run to establish the identity of all detectable mineral phases in the sample. The purpose of the preliminary analysis is to establish the scan range over which all subsequent samples of a suite will be analyzed. Normally one need not scan beyond  $90^{\circ}2\theta$ , inasmuch as the strongest Bragg reflections (those used for identification) are found in the "front reflection" direction (less than  $90^{\circ}2\theta$ ). The minerals normally present in most sediments or sedimentary rocks have the strongest lines at positions less than  $70-75^{\circ}2\theta$ . This point is practical and important when a large number of samples are to be analyzed: the longer the scan, the more time required for each analysis. The objective is to minimize the time required without jeopardizing the analysis. One of the best ways to accomplish this savings is to limit the scan range to that which will provide an analytical Bragg reflection for each identifiable mineral in the sample. If time is no problem, or if the sample is deemed important enough, a complete scan (at least up to  $90^{\circ}2\theta$ ) should be made.

Following the preliminary phase, the strongest Bragg reflection for each mineral phase is chosen for the analytical line. If the strongest Bragg reflection is interfered by a line from another mineral phase, the strongest uninterfered line is chosen as the analytical line. The analytical line is the Bragg reflection that will be monitored in every sample, and whose intensity will be used as a measure of the abundance of the particular mineral phase.

Most diffractograms are made with the goniometer scanning at  $1^\circ 2\theta$ /minute and the chart drive at 0.5 inch/minute. The diffractogram will therefore have a display of  $1^\circ 2\theta$  per 0.5 inch of chart, which provides adequate resolution for most analytical work.

A scale factor is chosen which increases the intensities of the minor mineral components to approximately half-scale, while the major components will be more than full-scale. This is done to facilitate recognition of minerals of low relative abundance. More often than not, the differences among different samples within a suite are not in the relative abundances of the major minerals, but rather in the relative abundances of the minor minerals.

Intensity measurements (either measured from the diffractogram or automatically measured by electronic integrators) are always integrated intensities, rather than absolute intensities. The integrated intensity is the area under the peak, whereas the absolute intensity is simply the height of the peak. If automatic integrators are used for intensity measurements, they are set to integrate from the background of the low-angle side of the peak to the background on the high-angle side. If intensity measurements are made from the diffractogram, the intensity is equal to the peak height times the width of the peak at one-half the height. For peaks that appear to be "clipped off" (a common observation), the true peak height is established by extending the two slopes of the peak until they intersect. (The true peak height is the distance from background to the intersection of the slopes.) The integrated intensity of a peak that goes "off-scale" can be determined by measuring the width of the peak at the base (the extension of the slopes to background), the width of the peak at 100 percent full-scale, and the distance from the base to 100 percent full-scale (height). The integrated intensity is then calculated by the relationship:

$$I_{int} = 0.5 \text{ height } \frac{(W_{base})^2}{W_{base} - W_{100\% \text{ F.S.}}}$$

The relationship assumes that a Bragg reflection is approximated by an isosceles triangle. The factor  $\frac{(W_{base} - W_{100\% \text{ F.S.}})}{\text{height}}$  gives

the rate of closure of an included isosceles triangle whose base is  $(W_{base} - W_{100\% \text{ F.S.}})$  and whose height is the measured height of the clipped (off-scale) peak (see Figure 1). Since the sides of the included triangle are parallel to the sides of the off-scale triangle (peak), if the  $W_{base}$  of the off-scale triangle is divided by the rate of closure of the included triangle, the quotient is the

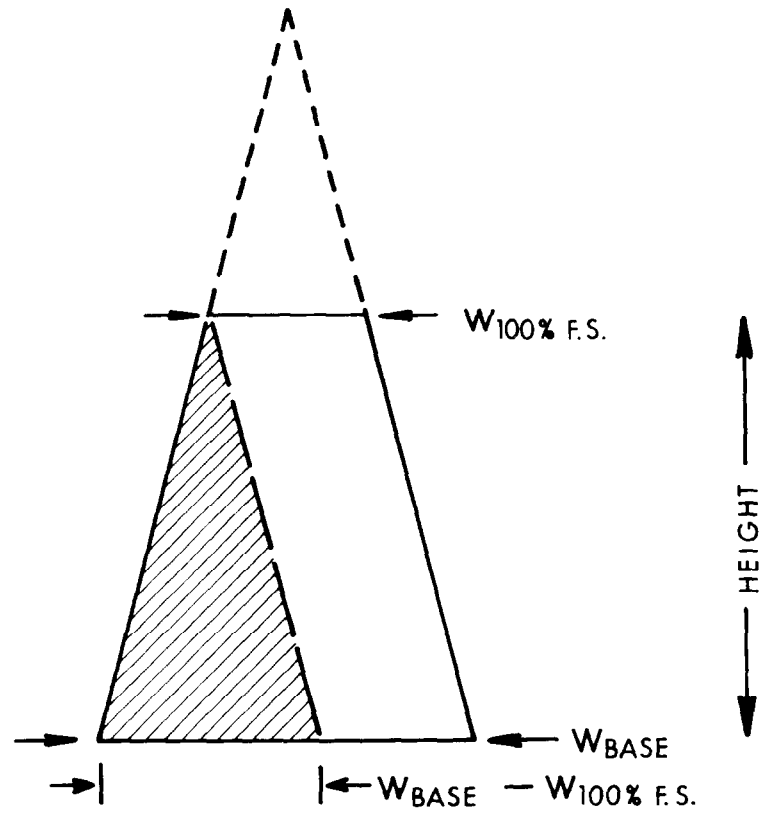


Figure 1. Estimation of the Height of an Off-Scale Diffraction Peak

calculated height of the off-scale peak. This value is then multiplied times  $\frac{1}{2} W_{\text{base}}$  to calculate the area under the off-scale peak.

The only correction made in the original data is for samples containing certain clay minerals. If the sample contains the mineral illite, the integrated intensity of the illite peak is multiplied by 2.5. (This factor takes into account the X-ray "reflectivity" or diffraction efficiency of illite which is, on the average, 2.5 times less than that of other clay minerals.) Also, if the sample shows 14Å clays (smectite, vermiculite, or chlorite) and kaolinite, the intensity of the 7Å position must be corrected. This is to compensate for the contribution to the 7Å position made by the (002) reflections of the 14Å clays, so that the true kaolinite intensity at 7Å can be determined. The amount of correction will depend on the specific 14Å clay and its relative abundance. It must also be noted that compositional variability in the makeup of the expandable clays (such as Fe-Mg substitutions in chlorite lattices) significantly affect the intensities of the basal reflections, and are recognized as inherent sources of error in the estimation of their abundances.

For a diffractogram, the individual integrated intensities of all the analytical peaks are summed, and the percent of total integrated intensity (%TII) represented by each analytical line is calculated. The %TII is the numerical measure of the abundance of the respective mineral phase. The %TII reported for a mineral in a mixture is proportional to the volume (or weight) percent of that mineral in the mixture. It is the purpose of this paper to demonstrate that the relationship between %TII and the "true" concentration of a mineral in a mixture is linear, and that the coefficient of proportionality (the slope of the linear regression line) is close to one.

#### EXPERIMENTAL DATA

The evidence to substantiate the premise of this paper is in the form of five sets of data. For each set of samples, quantitative X-ray diffraction data were collected following the procedures outlined above. The suites of samples were submitted by colleagues at the West Virginia University Department of Geology and Geography, the West Virginia Geological Survey, and ERDA-MERC.\* The X-ray data were collected independently of any analyses performed on the samples by the respective investigators. It was only after all data were collected that the comparisons described here were made.

The data sets represent a variety of different analytical problems and will demonstrate that the %TII values can be used to accurately estimate the true composition of the samples.

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\* MERC = Morgantown Energy Research Center, Morgantown, West Virginia.

### X-Ray Data Vs. Calculated API Values

(Data from Mujeeb Cheema, Department of Geology and Geography, West Virginia University.) Cheema submitted 15 Benson (Devonian) shale siltstone core samples. The samples were pulverized, ground, and pelletized by the procedure previously described, and analyzed for basic mineralogy (in particular, the clay mineralogy). Cheema had in the meantime calculated API values for the segments of the core from which the samples were taken. The API values are standard measurements of radioactivity calculated from gamma-ray-log data. The radioactive isotopes which are responsible for the gamma radiation are assumed to be contained within the clay-mineral assemblage. Assuming this to be true, there should be a relationship between the calculated API values and the total clay-mineral content reported for that segment of the core. The combined %TII's for all the clay minerals within each sample and the calculated API value for that sample are plotted in Figure 2. The figure shows the regression formula and the linear-correlation coefficient of 0.874. The correlation is good, considering that clay minerals are the most difficult to accurately quantify because of inherent variability in both composition and crystallinity.

### X-Ray Data Vs. Grain Density

(Data from Royal Watts, ERDA-MERC.) Twenty samples of the Mississippian Greenbrier Group (Big Injun) were submitted for bulk-rock mineralogical analysis. The X-ray analyses showed the samples are made up almost entirely of three mineral phases: calcite, dolomite, and quartz. From the %TII values reported for each mineral phase in each sample, Watts calculated grain-density values for each sample, using standard mineral-density values. In the meantime, the samples had been submitted to a commercial laboratory that determined the grain densities from standard physical tests. The data are compared in Table 1.

Table 1. Grain-Density Values

	<u>Grain Density</u> <u>X-Ray Data</u>	<u>Grain Density</u> <u>Commercial Lab</u>
MEAN VALUE	2.811	2.803
ABS STD DEV	0.022	0.022
REL STD DEV	0.774	0.794
ABS STD DEV MN	0.005	0.005
REL STD DEV MN	0.173	0.178

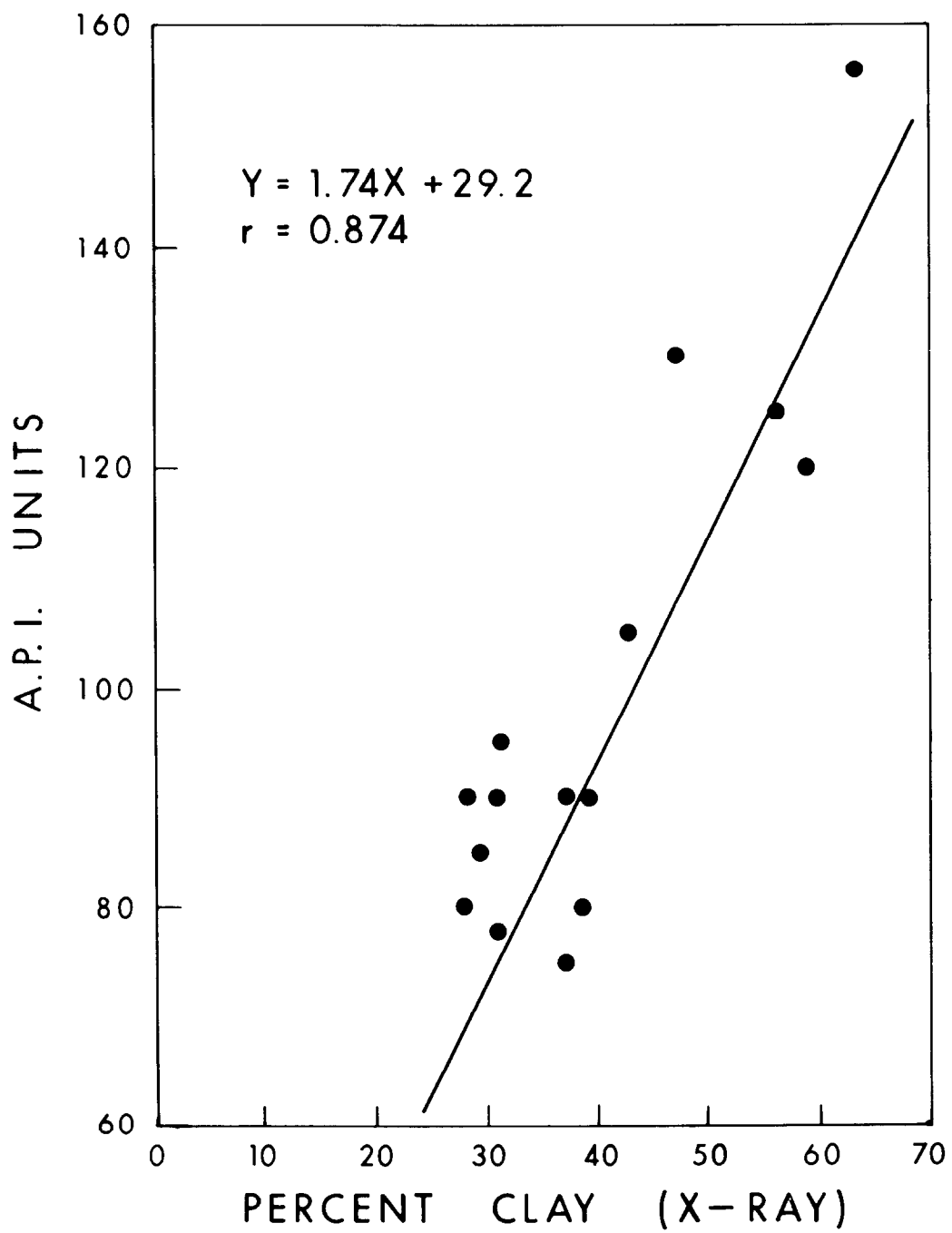


Figure 2. Percent Clay (X-Ray)  
Vs. A.P.I. Units (Cheema)

It is apparent without further statistical treatment that the two data sets are nearly identical. These data demonstrate that, at least with carbonates, the %TII values can be used to calculate grain densities. In addition, they demonstrate that the %TII values reported for each mineral phase must be numerically very close to the true volume (or weight) percent of the respective mineral phase in the rock.

#### X-Ray Data Vs. Carbonate Petrographic Data

(Carbonate samples and respective petrographic data from Richard Larese and Richard Smosna, West Virginia Geological and Economic Survey.) Larese's samples are of the Mississippian Greenbrier Group (Big Injun Interval), while Smosna's are Silurian Tonoloway Limestone. The two sample sets are extremes in composition and lithotypes: the Greenbrier samples are largely finely crystalline, sandy, oolitic dolomites, while the Tonoloway samples are argillaceous micritic limestones. Sixty samples were analyzed -- 18 of the Greenbrier and 42 of the Tonoloway. X-ray diffraction analyses were performed on whole-rock samples of each, and acid-insoluble residues were prepared for X-ray diffraction analyses.

Larese's petrographic analyses of the Greenbrier samples were performed using stained thin sections. The stain used was Alizarin red S, which preferentially stains calcite red. Larese's petrographic data showed three major components, dolomite, calcite, and quartz, with all but two samples being dolomite-rich. According to Larese, the sum total of the percentages of these three mineral phases, plus the percent porosity, accounts for 98-99 percent of the rock volume, indicating negligible clay-mineral content. The analyses of the acid-insoluble residues support these data. The X-ray analyses of the residues show that quartz is the dominant component in all the samples. Larese's data for calcite, dolomite, and quartz are plotted versus the respective X-ray data in Figures 3, 4, and 5.

Smosna's data were collected from unstained thin sections. Smosna also reported the same three mineral phases as the major components, with all but one sample being calcite-rich. The quartz content reported by Smosna ranges from "0" or "trace" up to 4 percent, with the exception of one sample for which he reported 8-percent quartz. The acid-insoluble residues of these samples, however, showed noncarbonate concentrations ranging up to 18 percent of the total rock. It was assumed, therefore, that much of the noncarbonate mineral composition was of such small particle size that it could not be observed by the microscopic technique. It was further assumed that the percentages of calcite and dolomite reported by Smosna were the true relative abundances of those mineral phases in the rock. Therefore, using the mineral concentrations as reported by Smosna and the acid-insoluble residue percentages, Smosna's calcite and dolomite values were corrected to take the residue into account by multiplying each percentage by [100 - acid-insoluble residue]. The X-ray data were then compared

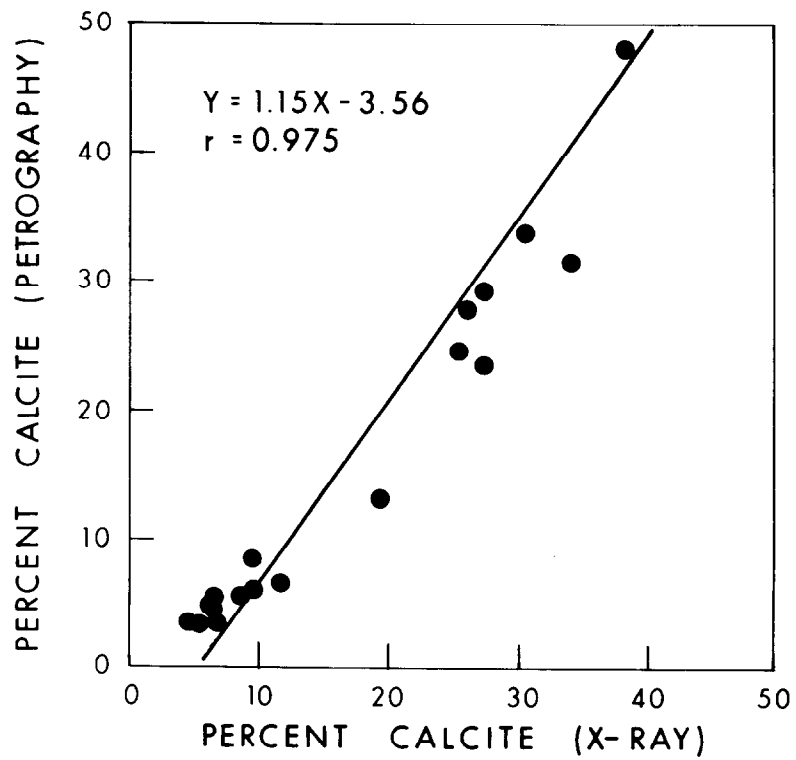


Figure 3. Percent Calcite (X-Ray) Vs. Percent Calcite (Petrography) for Greenbrier (Larese)

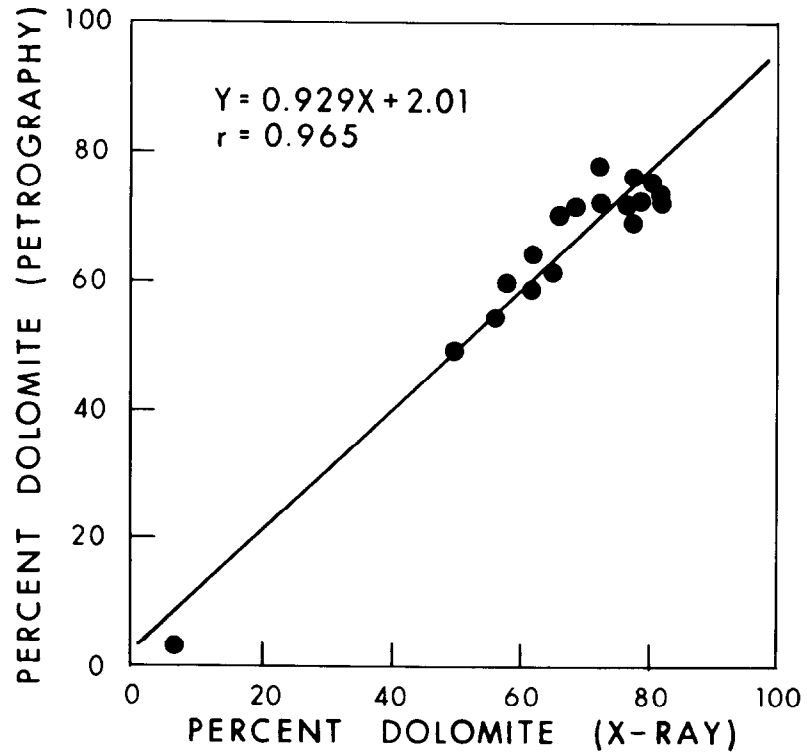


Figure 4. Percent Dolomite (X-Ray) Vs. Percent Dolomite (Petrography) for Greenbrier (Larese)



against the corrected petrographic data (see Figures 6 and 7).

A group of 11 samples as plotted on Figure 6 shows significant deviation from the X-ray data (open circles). In these samples, the petrographic calcite values are considerably higher than those reported by X-ray. Smosna (1977, personal communication) indicated that each of these samples contains exceedingly fine-grained dolomite, and as a result, significant errors could have been made in his measurements, i.e., over-estimation of the relative amount of calcite. Therefore, these 11 data points are not used in the statistical calculations that follow. They do, however, illustrate the difficulty of using the optical microscopic technique with fine-grained rocks, and the advantage of X-ray diffraction studies of such samples.

The statistical data for Smosna's samples are not as good as those for Larese's. However, the fact that Smosna's data are from fine-grained rocks may account for the low slopes and the deviation of the intercepts.

However, when the two data sets of Larese and Smosna are combined, the correlation between the petrographic data and the X-ray data is nearly perfect (Figure 8). A plot of the calcite/calcite + dolomite ( $c/c+d$ ) determined by X-ray and the petrographic technique for the combined data is shown in Figure 9. The data imply that uncorrected X-ray data from carbonate samples can be used to estimate the true mineral abundances with a high degree of accuracy and precision.

#### X-Ray Data Vs. Chemical Analyses for Recent Sediments

(Data from Edward Nuhfer, West Virginia Geological and Economic Survey.) The samples were clay-silt-sized suspended sediments collected in sediment traps at Morson Lake, the cooling water impoundment of the Arizona Public Service Company's Four Corners Power Plant near Farmington, New Mexico. The objective of the X-ray analysis was to determine the mineralogical composition of each sample. Samples were prepared for X-ray diffraction on Millipore filter mounts. Diffractograms revealed quartz and calcite as the sole crystalline components. While chemical analyses revealed considerable aluminum, no clay or feldspar peaks were noted. The aluminum was attributed to its presence in amorphous flyash, which consists of about 30-percent  $Al_2O_3$ .

Nuhfer additionally determined the calcite content of each sample by three independent techniques: (1) back calculation from calcium values obtained by atomic absorption spectrophotometry, (2) ignition (method of Dean, 1974), and (3) titration (method of Royse, 1970). The correlation between the values acquired from the titration and ignition techniques is graphically shown in Figure 10. The correlation between the values from A.A. back calculation and ignition determinations is shown in Figure 11.

The linear correlation between the data sets of any pair of

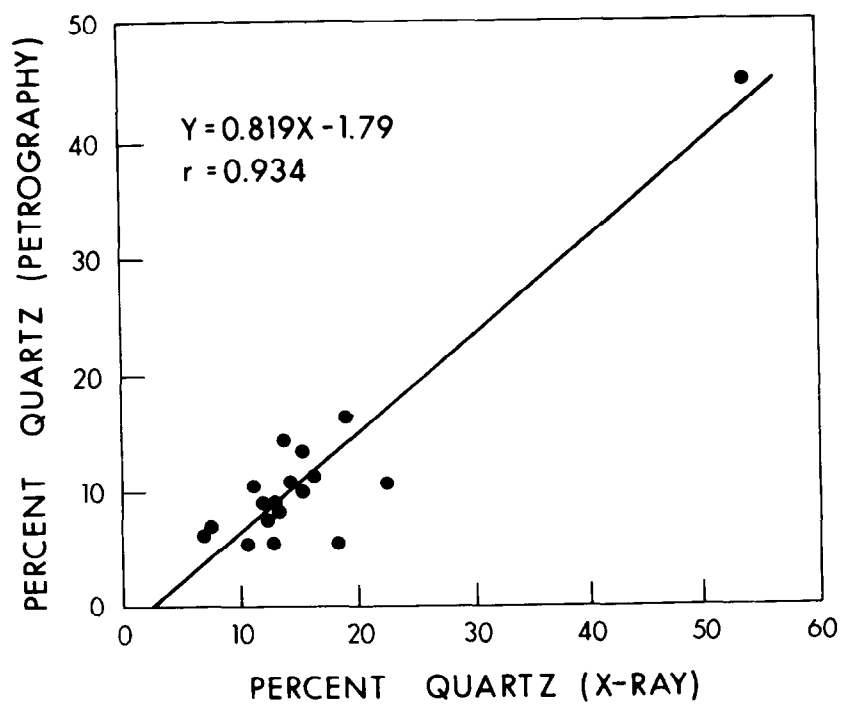


Figure 5. Percent Quartz (X-Ray) Vs.  
Percent Quartz (Petrography) for Greenbrier (Larese)

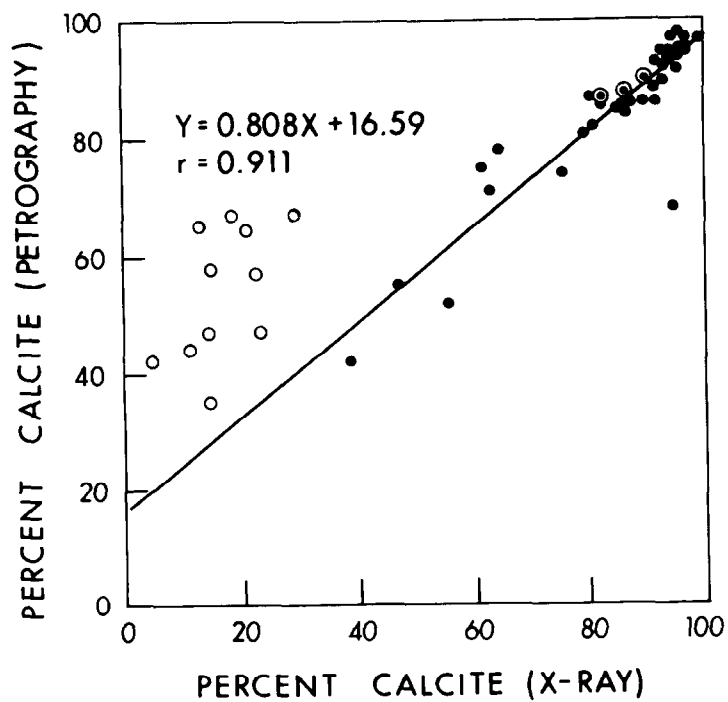


Figure 6. Percent Calcite (X-Ray) Vs.  
Percent Calcite (Petrography) for Tonoloway (Smosna)

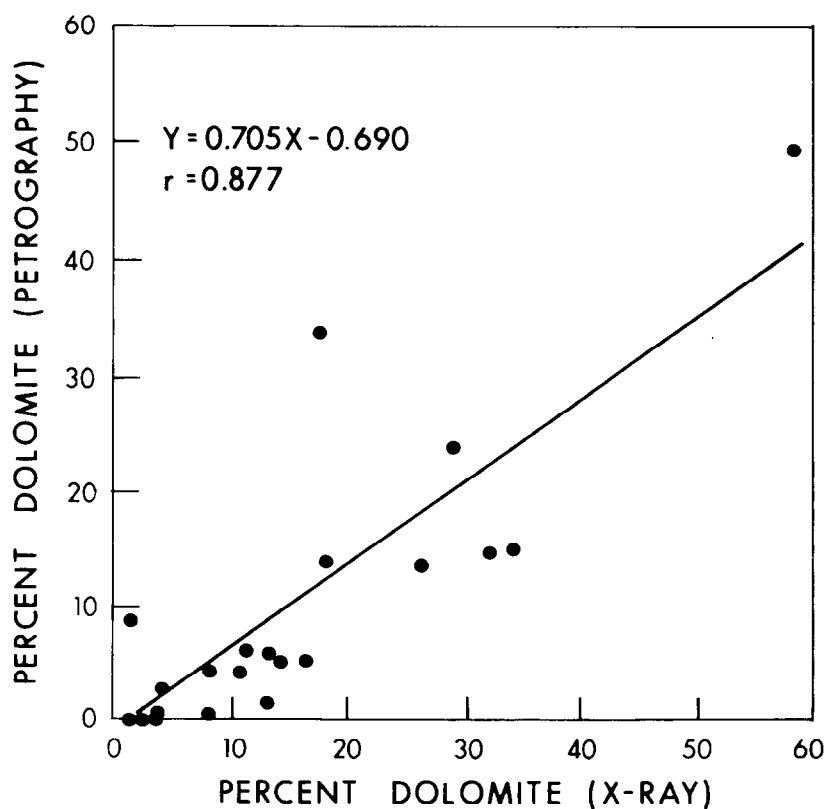


Figure 7. Percent Dolomite (X-Ray) Vs.  
Percent Dolomite (Petrography) for Tonoloway (Smosna)

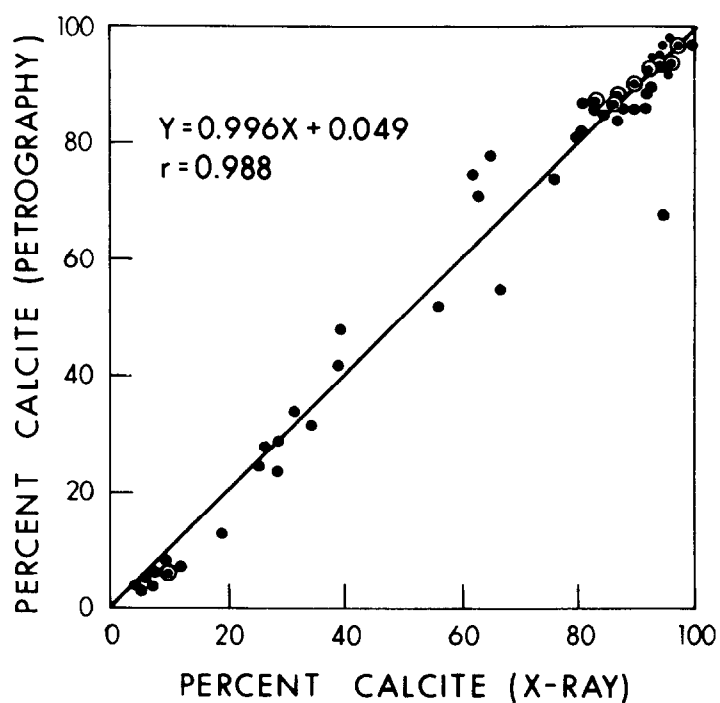


Figure 8. Percent Calcite (X-Ray) Vs.  
Percent Calcite (Petrography) for Greenbrier and  
Tonoloway (Laresse & Smosna)

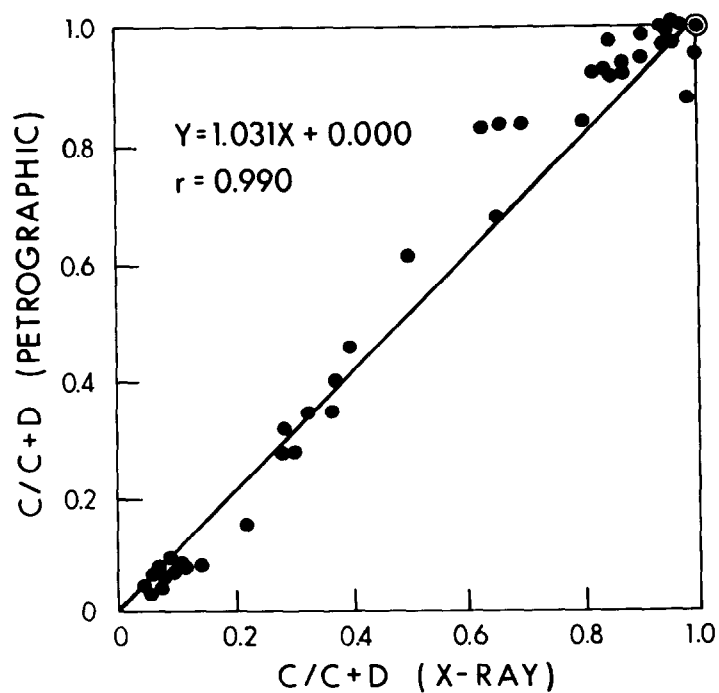


Figure 9. C/C + D (X-Ray) Vs. C/C + D (Petrographic) (Laresse & Smosna)

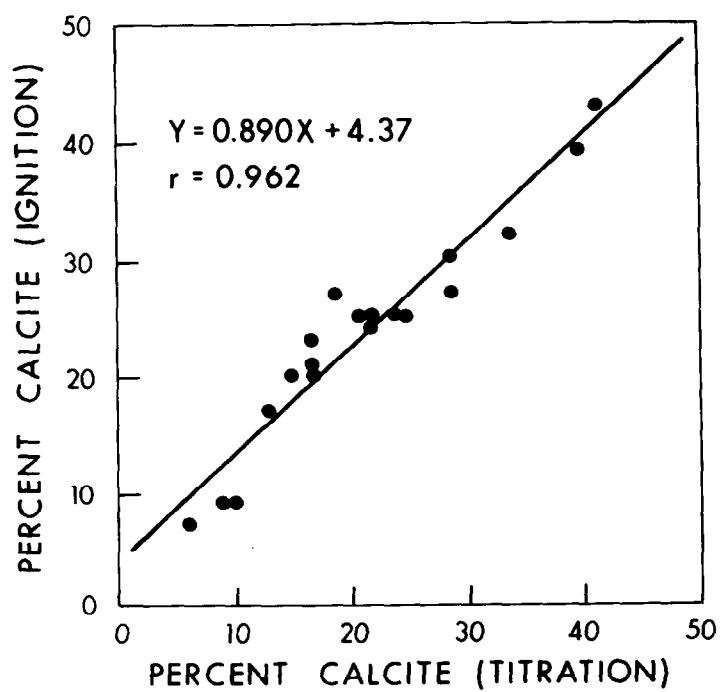


Figure 10. Percent Calcite (Titration) Vs. Percent Calcite (Ignition) (Nuhfer)

the four techniques ranges from 0.94 to 0.96. The plot of the X-ray data versus the A.A. back calculation (Figure 12) has a regression line with a slope of 0.49, which is explained by the high content of amorphous material. Nuhfer estimated the weight percent of amorphous material to average about 45 percent for these samples. The amorphous material includes, in order of abundance, glassy siliceous flyash from the nearby power plant, diatom frustules, and possibly amorphous clays.

## CONCLUSIONS

Any analytical determination is an estimation of the true abundance of compositional parameters. The degree to which any one technique estimates the true abundance is best evaluated by comparing the values produced to those of other proven and tested procedures. Agreement between procedures is not evidence of the accuracy and/or precision of either; they both could be equally wrong. However, such agreement implies strongly that the procedures both provide reliable estimates of the true abundance.

In this paper, I have demonstrated that uncorrected X-ray data is comparable to that generated by a number of compositional and compositional-dependent analytical procedures. Although circumstantial in nature, the evidence presented demonstrates that uncorrected X-ray data, reported as percent of total integrated intensity (%TII), provide abundance numbers which are directly proportional to the true abundance of the respective mineral phase, and that the coefficient of proportionality has a value of near unity. The key to the success of this technique is careful sample preparation.

Admittedly, these data were generated from samples (sedimentary materials) which do not show the wide range of composition, and therefore absorption properties, that may characterize igneous and metamorphic and some sedimentary rock materials. In the latter case, the value of the proportionality constant for a given mineral phase no doubt would depart from unity, and as a result, the %TII reported for a given mineral component would not be numerically equal to its abundance, i.e., the %TII would not necessarily give an absolute measure of abundance. However, it would still provide a measure of relative abundance which is adequate for most geochemical and geological applications. Stratigraphic and lateral facies could still be recognized and interrelationships with other compositional parameters could still be statistically evaluated.

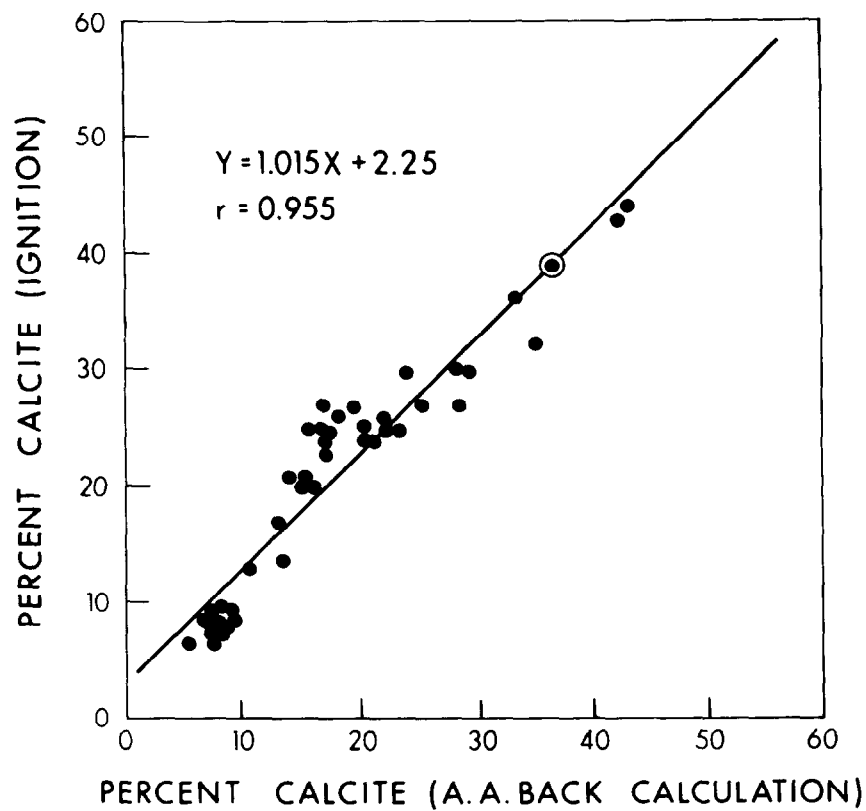


Figure 11. Percent Calcite (A.A. Back Calculation) Vs. Percent Calcite (Ignition) (Nuhfer)

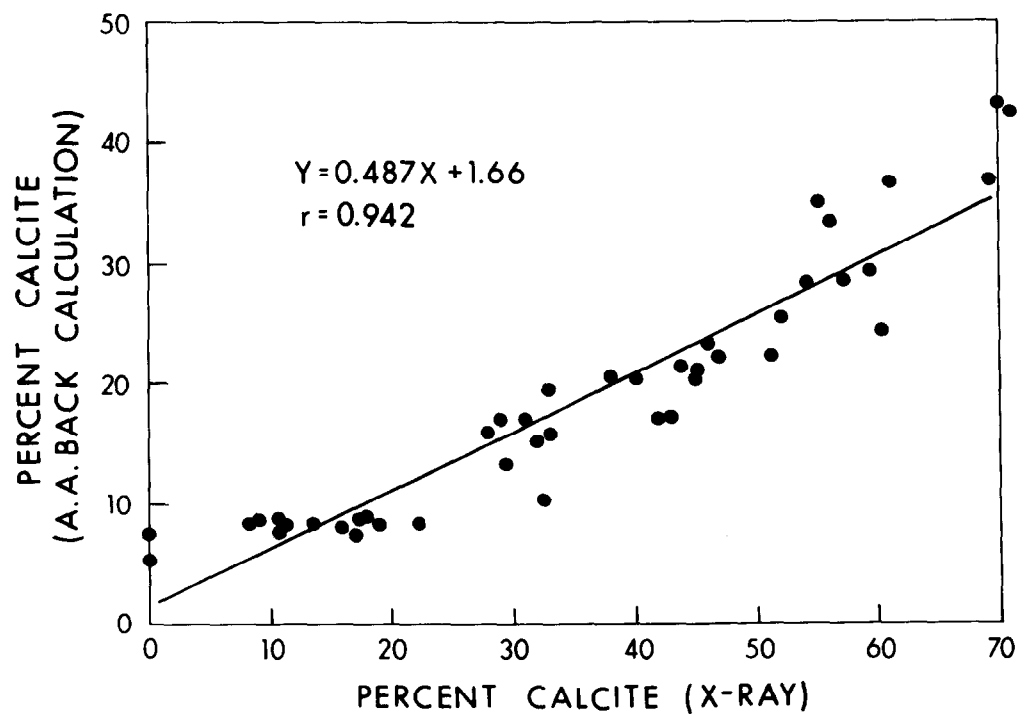


Figure 12. Percent Calcite (X-Ray) Vs. Percent Calcite (A.A. Back Calculation) (Nuhfer)

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